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History of Sulfur Content Effects on the Thermal Stability of RP-1 Under Heated Conditions

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Abstract

As technologies advance in the aerospace industry, a strong desire has emerged to design more efficient, longer life, reusable liquid hydrocarbon fueled rocket engines. To achieve this goal, a more complete understanding of the thermal stability and chemical makeup of the hydrocarbon propellant is needed. Since the main fuel used in modern liquid hydrocarbon systems is RP-1, there is concern that Standard Grade RP-1 may not be a suitable propellant for future generation rocket engines due to concern over the out dated Mil-Specification for the fuel. This current specification allows high valued limits on contaminants such as sulfur compounds, and also lacks specification of required thermal stability qualifications for the fuel. Previous studies have highlighted the detrimental effect of high levels of mercaptan sulfur content (~50 ppm) on copper rocket engine materials; but, the fuel itself has not been studied. While the role of sulfur in other fuels (e.g., aviation fuel, diesel, and automotive) has been extensively studied, little has been reported on the effects of sulfur levels in rocket fuels. Lower RP-1 sulfur concentrations need to be evaluated and an acceptable sulfur limit established before RP-1 can be recommended for use as the propellant for future launch vehicles.

Introduction

Liquid rocket engines face extremely challenging thermal environments, and almost inevitably require copper or copper alloys in construction due to their high thermal conductivity properties. It has long been known that sulfur compounds and copper are incompatible; but a better understanding of RP-1's thermal stability and chemical interaction with copper chamber liners is needed. Previous research has shown that when RP-1 begins to thermally decompose and "coke" inside the chamber, (usually between 600 and 900°F)[9] the deposits formed contain a noticeable amount of copper sulfide (Cu_2S). This phenomena has been attributed to sulfur compounds contained within the fuel reacting with the wetted copper walls. The main concern over this reaction is that as the Cu_2S is formed, it leaves "pits" or "craters" in some sections of the liner wall and flow obstructing particle "barnacles" in other areas. Carbon deposits now have a rough surface finish to adhere to in the chamber, which contributes to increasing localized wall temperature and further coking. The total effect leads to increased pressure drop in the system, decreased efficiency, and loss of structural integrity--possibly resulting in engine failure.

Solutions for preventing the buildup of copper sulfide in the chamber include decreasing the amount of allowable sulfur contained in the fuel during production, or using other acceptable channel wall materials with suitable liner coatings. In order to accept either of these solutions, more information must be gathered regarding sulfur content and material compatibility. Currently, there is an ongoing joint research effort between NASA and the Air Force Research Laboratory (AFRL) examining the effect of sulfur content in the new grades of RP-1, TS-30 (<30ppm total sulfur), TS-5 (<5ppm total sulfur), and UL RP-1 (<0.1ppm

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14. ABSTRACT
As technologies advance in the aerospace industry, a strong desire has emerged to design more efficient, longer life, reusable liquid hydrocarbon fueled rocket engines. To achieve this goal, a more complete understanding of the thermal stability and chemical makeup of the hydrocarbon propellant is needed. Since the main fuel used in modern liquid hydrocarbon systems is RP-1, there is concern that Standard Grade RP-1 may not be a suitable propellant for future-generation rocket engines due to concern over the outdated Mil-Specification for the fuel. This current specification allows high valued limits on contaminants such as sulfur compounds, and also lacks specification of required thermal stabiity qualifications for the fuel. Previous studies have highlighted the detrimental effect of high levels of mercaptan sulfur content (~50 ppm) on copper rocket engine materials; but, the fuel itself has not been studied. While the role of sufur in other fuels (e.g., aviation fuel, diesel, and automotive) has been extensively studied, little has been reported on the effects of sulfur levels in rocket fuels. Lower RP-1 sulfur concentrations need to be evaluated and an acceptable sulfur limit established before RP-1 can be recommended for use as the propellant for future launch vehicles.

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total sulfur). A range of thermal stability experiments, including recently completed tests in the NASA Glenn Heated Tube Facility (HTF) and upcoming tests in the AFRL High Heat Flux Facility (HHFF), are planned using each of the fuels and both OFE and GRCop-84 materials. Sub-ppm sulfur speciation and concentration measurements are being made at the Analytical Laboratory, Edwards AFB using the ASTM D-5623 method.

RP-1's specification (MIL–P-25576C) was established in the mid 1950's to provide a consistently suitable propellant for rocket engines rather than the kerosene based fuels available at that time (JP-4, 5) for jet engines. RP-1 is also kerosene based fuel, but with a narrower allowable density range and it has lower limits on various fuel components than existed for JP-4, 5 at that time. Since then, technology has improved and the jet fuel community has developed more thermally stable and "cleaner" burning fuels for use in turbine engines (JP-7, 10, 8 and 8+100), but little has been achieved with regards to rocket propellants. Some minor cosmetic changes to the specification were made in 1957 and 1967 and larger changes made in 1982, when an adjustment to the acceptable density range, an addition of a particulate test standard, and an increase in the allowable olefin content (from 1% to 2%) was made. It's worth noting that this update in 1982, while increasing the available number of RP-1 suppliers, actually served to decrease the overall thermal stability of RP-1 because the allowed increase in olefin content generally leads to increased deposit formation.

Eighty-seven different hydrocarbons have been identified in RP-1, and as expected in a batch refined product, the composition of the fuel can fluctuate between batches. The main constituents found in RP-1 are the desirable hydrocarbons like paraffins and naphthenes, and the undesirable components such as aromatics, olefins, sulfur compounds, and other trace ingredients remaining from the refining process. These undesirables increase occurrences of coking and corrosion, and can cause "gumming" in the fuel "cooling" channels, all of which are harmful to the overall life and efficiency of the engine. Table 1 shows a comparison between RP-1 and other common hydrocarbon propellants.

Previous Research

To date, limited data exists in the rocket fuel community that quantifies the effects that RP-1 has on copper cooling channels. From the mid-1980's to early 1990's, however, several facilities were established and research conducted to simulate fluid flow behavior in rocket engine cooling channels. Research using these facilities also focused some effort towards attempting to quantify sulfur content in fuel and the effect it has on cooling channel materials degradation.

United Technologies Corporation

One of the first of these simulative rocket facilities was constructed by United Technologies Research Center (UTRC). During UTRC's heated tube experiments in the mid 1980's, they experimented using a tube consisting of 99.99% pure copper liner surrounded by an outer Inconel 600 tube. This dual tube construction provided the required tensile strength for the outside of the tube during high temperature testing; while still wetting a copper surface. To observe copper-sulfur interactions, UTRC added thianaphthene and benzyl disulfide to RP-1, creating a total sulfur concentration in the fuel samples of 0.05 wt%, the maximum limit as stated in MIL–P-25576C . UTRC used a 13.8 MPa inlet fuel pressure, 30 m/s velocity, 290 K temperature, and test duration of 10 minutes as a baseline for all their experiments, all of which are approximately simulative of modern rocket nozzle design conditions. Results obtained from the sulfur addition indicated that the high levels of sulfur in the fuel accelerated contaminate deposition rate and tube corrosion; however, it was also determined that additional research in this area was required before a definite result could be concluded.[2]

UTRC's results begin to illustrate how detrimental sulfur content can be when used in a system containing copper. From these results it is also indicated that the upper limits on sulfur content within the current RP-1 specification might be too high for an acceptable limit. Further investigation would help determine exactly what RP-1 sulfur levels would be considered acceptable for use in future engines.

Property	RP-1	JP-4	JP-5	JP-7	JP-8	JP-10
Distillation:						
Initial Boiling Point (°C)	TBR	TBR	TBR	182	TBR	
10% Recovered (min) (°C) (max) (°C)	185 210	TBR	 205	196	205	
20% Recovered (°C)		100	TBR	206	TBR	
50% Recovered (°C)	TBR	125	TBR	TBR	TBR	
90% Recovered (°C)	TBR	TBR	TBR	260	TBR	
End Point (max) (°C)	274	270	300	288	300	
Residue (vol% max)	1.5	1.5	1.5	1.5	1.5	
Loss (vol% max)	1.5	1.5	1.5	1.5	1.5	
Gravity API—min (sp. gravity max)	42.0 (0.815)	45.0	36.0	44.0	37.0	 (0.943)
Gravity API—max (sp. gravity min)	45.0 (0.801)	57.0	48.0	50.1	51.0	(0.935)
Existent Gum (mg/100mL, max)	7	7.0	7.0	5.0	7.0	5.0
Sulfur (total wt%, max)	0.05	0.40	0.30	0.1	0.30	
Mercaptan-sulfur (wt%, max)	0.005	0.002	0.002	0.001	0.002	
Freezing Point (max) (°C)	-38	-58	-46	-43.3	-47	-79
Heat of Combustion (lower) (min) (MJ/kg)	43.0	42.8	42.6	43.5	42.8	42.1
Viscosity (max)	16.5 mm^2/s @-34°C	-------	8.5 mm^2/s @-20°C	8.0 mm^2/s @-20°C	8.0 mm^2/s @-20°C	40 mm^2/s @-54°C
Aromatics (vol%, max)	5.0	25.0	25.0	5	25.0	
Smoke Point (mm, min)	25.0	20.0	19.0		25.0	
Flash Point (min) (°C)	43	----	60	60	38	54.4
Particulate (max) (mg/L)	1.5	1.0	1.0	Origin 0.3 Destination 0.5	1.0	1.0
Vapor Pressure		2.03 psi @37°C (min) 3.05 psi @37°C (max)	-----	3.0 psi @149°C (min) 48.0 psi @260°C (max)		

Table 1: Military Specification Comparison of Commonly Used Propellants

Aerojet Corporation

Following the work performed by UTRC , Aerojet constructed their own facility and conducted experiments with various sulfur species and hydrocarbon fuels. This facility, the Aerojet Carbothermal Rig, was operational in the late 1980's and early 1990's. Initially, Aerojet performed static tests to determine material compatibility of various copper alloys (OFHC, NASA-Z, and Amzirc copper) with four hydrocarbon fuels, RP-1, n-dodecane (a sulfur free hydrocarbon intended to simulate a "pure-grade" RP-1), methane, and propane. Two types of static tests were conducted; the sealed glass ampule test for RP-1 and n-dodecane, and the Aminco bomb test for methane and propane compatibility. All the ampule experiments were loaded and sealed, then heated to 400°F for fourteen days. The Aminco tests were brought up to 650°F and 3000 psia, and then held at these parameters for 30 minutes. Each of these tests had a control sample and a sample spiked with the sulfur compound n-dodecanethiol. The results from these static tests show that the copper coupons which were exposed to the control samples were basically unchanged, whereas the coupons exposed to the sulfur contaminated fuel were severely tarnished. This was attributed to the formation of copper sulfide (Cu_2S).[6]

The sulfur/copper reaction attacks grain boundaries of the wetted walls, pushing Cu_2S dendrites into the flow, restricting fluid flow through the channel and serving to increase pressure drop and increase available surface area for continued deposition. This grain boundary attack is demonstrated in Figure 1, as depicted by Homer, et al of Aerojet.[3] In this figure,

image 'a' shows initial formation of Cu_2S on the channel wall, and image 'b' depicts how the Cu_2S has begun to penetrate the copper grain boundaries. In an attempt to refurbish the test sections, Aerojet rinsed the test section walls with a dilute NaCN (3-5% w/w) solution during their post-test analysis. After the rising, it was seen that the surface finish became pitted and rough and that some of the copper material was removed from the channel wall (image 'c'). [3]

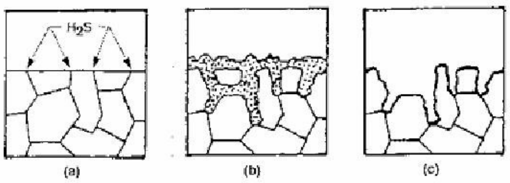


Figure 1: Representation of Grain Boundary Attack, Penetration, and Removal[4]

In dynamic testing using the Aerojet Carbothermal Rig the significance of sulfur was examined. During the test, 50 ppm of mercaptan sulfur was added to RP-1, subsequently exceeding the maximum allowable limit stated in the RP-1 specification. At a wall temperature of 308 °C (~586°F) and duration of 2339 seconds, it was observed that the interior copper walls were severely corroded and that copper residue was found both in the filter and the post-test fuel samples. The SEM pictures taken of the channel show a roughening of the channel surface. When magnified, there appeared to be "barnacles" of copper sulfite growing out of the channel wall. (Figure 2) This was in contrast to results from similar tests with undoped RP-1.

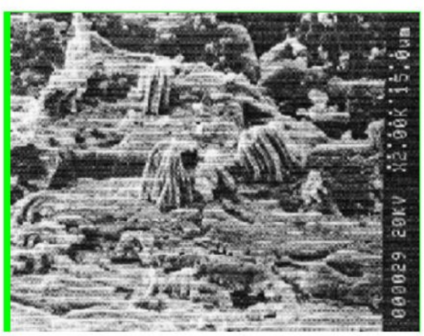


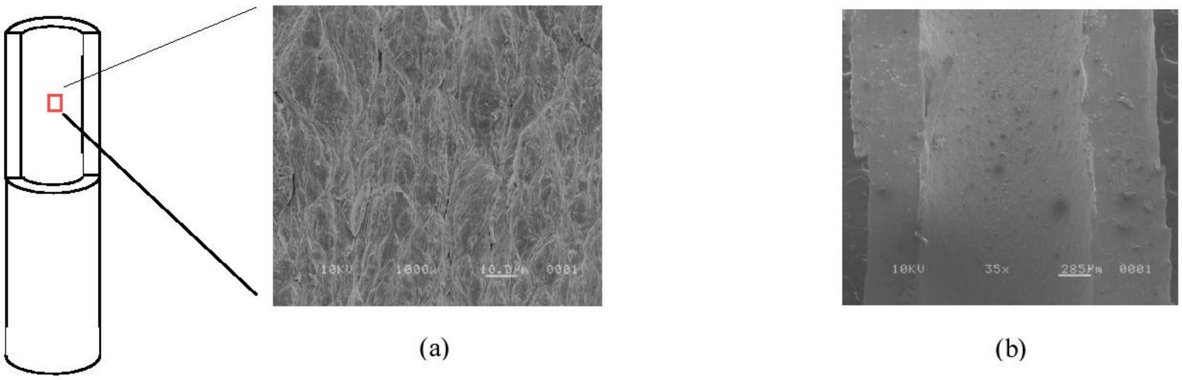
Figure 2: SEM Images of Cu_2S "Barnacle" Growth on Wetted Copper Channel Walls[4]

These Cu_2S barnacles also appeared when methane was contaminated with sulfur, namely the odorant methyl mercaptan. In the experiments run using methane, three different concentrations of sulfur were used, 200 ppm, 10 ppm, and 1 ppm, all by volume. All concentrations caused corrosion and formation of copper sulfide within the channel. A severe reduction in flow was seen with 10 ppm sulfur addition, and total blockage of the channel occurred with the 200 ppm sulfur level. When the fuel channels were examined by EDX (Energy Dispersive X-Ray scattering) the deposits were found to consist of only copper and sulfur. The experiments conducted using propane were inconclusive due to an inability to obtain "sulfur-free" propane for a baseline.[3,6]

Aerojet's experiments and findings, like those of UTRC, are vital in aiding the understanding of sulfur contamination in hydrocarbon fuels. Aerojet's results begin to quantify what level of sulfur contamination in hydrocarbon fuels is acceptable for use in copper cooling channels. They also demonstrate how detrimental the Cu_2S growths can be to the system.

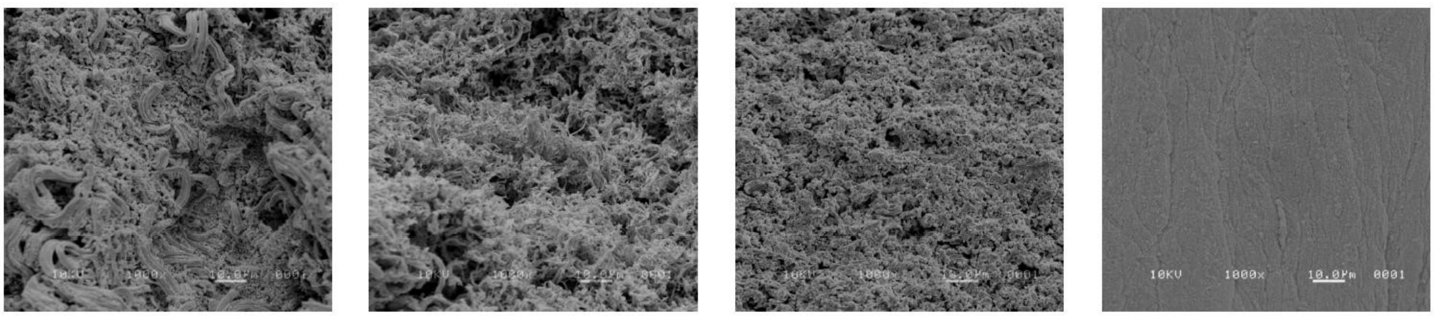
NASA

More recent tests were conducted at the NASA Glenn Research Center's Heated Tube Facility.[7, 8] Five liquid hydrocarbon aerospace fuels (JP-7, JP-8, JP-8+100, JP-10 and RP-1) were tested for heat transfer and thermal stability characteristics in both OFE copper and stainless steel test 304 sections. Figure 3 (a) shows a clean section of a copper test section and (b) sulfur accumulation obtained during a run using JP-8 and 304 SS. Due to differences in their specifications and manufacturing processes, the kerosene fuels had total sulfur contents ranging from 2 to 400 ppm. JP-10 was not analyzed for sulfur. The tests were operated at 750 °F and 1000°F average wall temperatures and 25 and 75 ft/sec flow velocities for a 20-minute nominal duration. The higher sulfur content fuels, JP-8 & JP-8+100, showed significant differences greater deposit formations in the copper test sections, as shown in Figures 4, and 5. The deposits were also evident in the heat transfer and pressure drop behavior during the tests. The highest wall temperature and lowest velocity tests were terminated after only a few minutes because the test sections were nearly plugged. Subsequent microscopic and EDS analysis indicated large amounts of copper sulfide formations were formed. Even in the RP-1 test sections with ~23 ppm sulfur, it appeared that copper sulfide nodules were formed. (Figure 6) No evidence of copper sulfide formation was observed in the JP-7 test sections, although a small amount of carbon deposit was present. Figure 7 shows copper test section internal surface micrographs (1000X magnification) for a clean copper tube section and post test sections run using JP-8, RP-1, JP-7, and JP-10 respectively



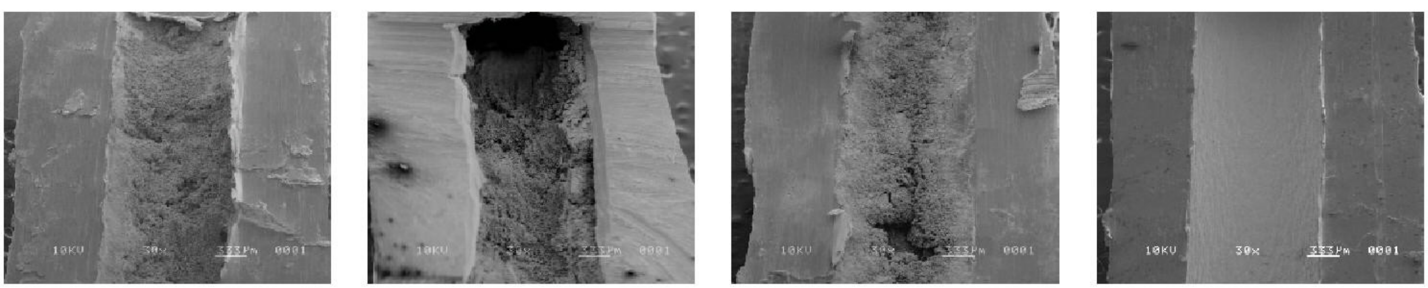
(a) (b)

Figure 3: (a) Figure 3. SEM micrograph of a clean section of Copper 101 tubing showing the as delivered internal surface due to the drawing process and (b) Interior surface of SS 304 tube (magnification 35x) tested with JP-8 for 20 minutes; 75 ft/s, 1000 °F.



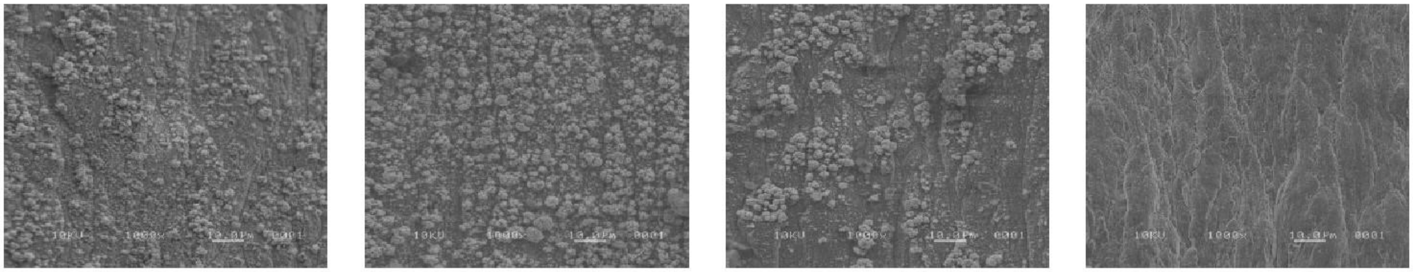
(a) (b) (c) (d)

Figure 4: Copper test section internal surface micrographs (1000X magnification) at various distances into the heated portion of the tube; JP-8 fuel, sulfur content 400 ppm, 2 minute test duration. (a) 1.5 inches; (b) 4 inches; (c) 6 inches; (d) tube outlet down stream of heated section



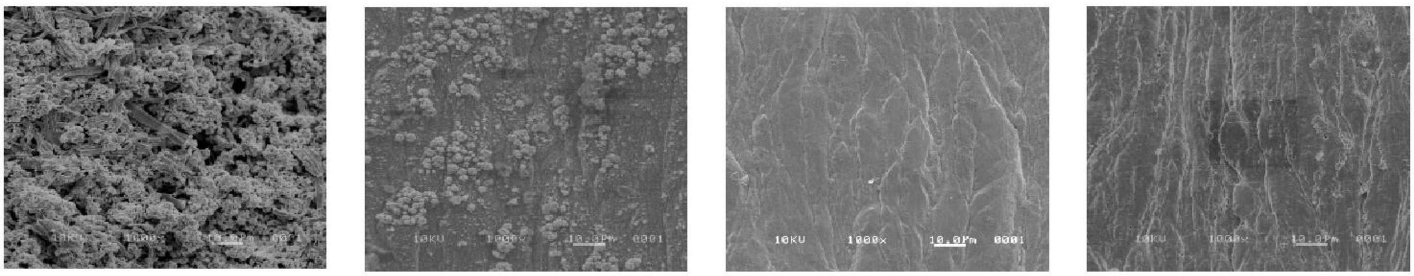
(a) (b) (c) (d)

Figure 5: Copper test section internal surface micrographs (30X magnification) at various distances into the heated portion of the tube; JP-8 fuel, sulfur content 400 ppm, 2 minute test duration. (a) 1.5 inches; (b) 4 inches; (c) 6 inches; (d) tube outlet down stream of heated section



(a) (b) (c) (d)

Figure 6: Copper test section internal surface micrographs (1000X magnification) at various distances into the heated portion of the tube; RP-1 fuel, sulfur content 23 ppm, 20 minute test duration. (a) 1.5 inches; (b) 4 inches; (c) 6 inches; (d) tube outlet down stream of heated section



(a) (b) (c) (d)(d)

Figure 7. Copper test section internal surface micrographs (1000X magnification), 6 inches into the heated portion of the tube. (a) JP-8 fuel, sulfur content 400 ppm, 2 minute duration; (b) RP-1 fuel, sulfur content 23 ppm, 20 minute duration; (c) JP-7 fuel, sulfur content 10 ppm, 20 minute duration; (d) JP-10, sulfur content not analyzed (expected < 5 ppm), 20 minute duration

Lockheed Martin Corporation

As mentioned previously, another solution for eliminating the problems associated with sulfur contamination in RP-1 is to replace RP-1 with a better system fuel. One possible alternative fuel for exploration is Russian kerosene, more commonly known in the U.S. as RG-1. Lockheed Martin Astronautics conducted a comparative study between RP-1 and the Russian kerosene, also called "naphthyl," "naphtil," "naftin," and НАФТИЛ in Russia.[1] Lockheed conducted two types of studies on the fuels, static laboratory analyses and dynamic hot fire testing. The laboratory experiments consisted mainly of researching available technical literature on refinery and military specifications, and running elemental analysis to determine fuel characteristics. From Lockheed's analytical testing, it was found that RG-1 differs slightly in composition from RP-1 in both density and sulfur content. RG-1 has a 21% lower overall sulfur content than RP-1, and the Russian fuel also has no allowable mercaptan content. Differences between the two fuels are shown in Table 2. Lockheed's hot fire experiments were conducted using a portable 100 pound thrust stand with LOX / RP-1 and LOX / RG-1. Results from their hot fire testing show a significant increase in C* efficiency when the Russian kerosene was used in low mixture ratios (~1.9) versus the RP-1 at the same conditions.[4] This improvement in C*, coupled with the lower sulfur content contained in the Russian kerosene, makes RG-1 a viable alternate for RP-1.

Requirement	Russian	MIL-P-25576C2
Initial Boiling Point, °F	383 min	No requirement
10% Evaporation Temp, °F	410 max	365-410
50% Evaporation Temp, °F	455 max	No requirement
90% Evaporation Temp, °F	500 max	No requirement
Evaporation End Point Temp, °F	518 max	525 max.
Specific Gravity	0.830-0.836 at +20C	0.799-0.815
Total sulfur, wt. %	0.01	0.05
Total mercaptan, wt. %	None allowed	0.005
Total H_2S, wt. %	None allowed	No requirement
Freezing Point, °F	-76 max	-36 max.
Kinematic viscosity, CS at 68 °F	2.5 min.	No requirement
Kinematic Viscosity, CS at –30 °F	No requirement	16.5 max
Kinematic Viscosity, CS at –40 °F	25 min.	No requirement
Aromatics, %	5.0 mass max	5.0 vol. max
Olefins, %	No requirement	2.0 vol max
Smoke Point, mm	No requirement	25.0 min
Flash Point, °F	140	110 min

Table 2: Property Comparison between Russian Kerosene and Standard Grade RP-1

Suggestions for Improvement

Within the rocket community, there are several remedies for solving the incompatibility between copper and RP-1. One possible solution is to change the cooling channel material. Most materials and cooling schemes for liquid rocket engines used today rely on the large thermal conductivity of copper to keep wall temperatures below failure limits. Since copper typically has adverse reactions with Standard RP-1, new materials, such as NASA's GRCop-84 which is being explored as a possible cooling channel material, also require material compatibility evaluations. Another possible choice for future engines is adding a protective coating over the copper in the channels. However, many coating materials themselves need to be made compatible both chemically and thermally with the engine design and fuel. The main problems associated with using liners are the increased complexity of manufacturing, the added cost, and the risk that thermal cycling of the liner material may lead to spalling (i.e. the liner coating must be prime reliable for the life of the system). Any coated chamber may also require increased maintenance and inspection to ensure desired safety.

A second possible solution to the RP-1/sulfur reaction problem is to modify the specification of RP-1 by decreasing the total sulfur content allowed, and possibly even eliminating mercaptan sulfur completely. Additionally the elimination of olefin and aromatic components may increase thermal stability of the fuel by removing potential gum forming species. These types of eliminations will have to be conducted by the manufacturer of RP-1 during the refining process of the fuel if the contaminates are already present in the starting crude material. This will add cost and time to the refining process which will be reflected in higher overall fuel costs.

A third possible solution within the rocket community for this sulfur incompatibility problem is the use of additive packages to enhance the thermal stability of RP-1. This type of chemical additive solution has yet to be done for rocket propulsion, but is now common in the jet (turbine engine) based propulsion community. For example, the "+100 package" has been successfully added to JP-8, allowing an increase of 100 degrees in fuel operating temperatures with the added effect of prevention of coking in fuel lines and fuel spray nozzles. These packages seek to deactivate metal surfaces and contaminants, scavenge radical species, act as hydrogen donors, and/or provide anti-oxidants. Although chemical time scales and thermal environments of rocket engines vary widely from turbine engines, the development of a rocket fuel specific additive package could have a major benefit to rocket engine life by reducing the operational wall temperatures.

Current Efforts

In response to AF and NASA requests, the Defense Energy Support Center (DESC) has contracted with Haltermann Chemical Products, the current supplier of RP-1, to develop three new grades of RP-1: TS-30 (Total Sulfur-30) which contains <30ppm total sulfur, TS-5 (Total Sulfur-5) which contains <5ppm total sulfur, and Ultra-Low (UL) RP-1 which contains <100ppb of total sulfur. These new fuels were recently tested in NASA Glenn's Heated Tube Facility (HTF) for performance, tube material compatibility, and channel corrosion.[7] These fuels will also be tested at the AFRL's High Heat Flux

Facility, as part of a joint effort under NASA's RS-84 program.

Fuel Cooling Simulations

NASA Glenn's HTF ran several experiments testing the interaction of three grades of RP-1 (current production RP-1, TS-5, and UL) with OFE copper and GRCop-84, a copper alloy containing chromium and niobium. The average operating parameters for these experiments were a 675°F inner wall temperature, 75 ft/sec flow velocity, 3.8 BTU/in^2-sec heat flux, 1000 psig pressure, and with test durations ranging from 20 minutes to five hours. The results from the OFE copper tests showed the same type of results that were seen in earlier experiments performed by UTRC, Aerojet, and NASA. The standard grade RP-1 showed carbon deposition with a strong likelihood of copper sulfide formation. Crystallography on the NASA test sections was inconclusive due to a lack of available samples. In these tests a local increase in wall temperatures occurred concurrently with a large pressure drop. GRCop-84 wall material tests indicated that more deposits formed on this material than the OFE copper.

The experiments run using the TS-5 fuel appeared to eliminate the deposit formations, but increases in local wall temperature and pressure drop in the tube still occurred. When the UL fuel was tested, minimal deposits were observed in the tube and during the experiment a minimal temperature increase and pressure drop was detected. These findings are summarized in Table 3. Results using GRCop-84 as the tube material followed the same trends as OFE copper, except that higher levels of carbon deposition were detected in the GRCop-84 than in the copper sections.

Fuel	Deposit Formation	Localized Wall Temperature Increase	Pressure Drop
Standard Grade RP-1	Yes	Yes	Yes
TS-5	Reduced	Yes	Yes
UL	Minimal	Minimized	Minimized

Table 3: Summary of NASA Glenn HTF RP-1 Grade Findings

NASA's HTF findings, like Aerojet's and UTRC's, show that there is a correlation between sulfur content in fuel, Cu_2S formation and wall pitting. Further work needs to be conducted to determine if the new grades of RP-1 would be a beneficial replacement for the current grade. Also, the thermal stability and sulfur content of the new grades of RP-1 need to be investigated further. Continuing the research on advanced channel materials is also critical for development of future hydrocarbon rocket engines, since advanced materials could have significantly better performance than traditional rocket engine copper alloys.

Fuel Analysis

In addition to using simulative facility testing, another way to better understand how fuel will behave in a stressful environment is to study and model its chemical makeup. In the case of RP-1, interest is focused on quantifying and speciating sulfur content. AFRL's Analytical Laboratory at Edwards AFB has recently developed the capability to begin speciating and measuring total sulfur content in hydrocarbon fuels. Most of their effort is focused on testing all grades of RP-1. The analysis is performed by using a Sievers Model 355 SCD (Sulfur Chemiluminescence detector). The instrument is operated by first injecting the standard/sample into a gas chromatograph chamber. As the sample's components separate and elute off the column, they enter an 800°C furnace where all sulfur containing compounds are combusted to form sulfur monoxide (SO), water, and other products. The SO is then mixed with ozone in a reaction cell to produce excited state sulfur dioxide and oxygen. Chemiluminescence at <400 nm is detected by a blue-sensitive photomultiplier tube (PMT). Since all sulfur atoms are converted to SO_2 quantitatively, equimolar response is produced in the form of a chromatogram. The results obtained are then compared to known concentrations of standards (created by ASTM method D-4307) that are run under the same parameters as the samples. A UV pass filter (225-450 nm) and efficient combustion in the ceramic tubes of the furnace eliminate interference from non-sulfur containing analytes that also undergo chemiluminescent reactions with ozone.

The Sievers Model 355 SCD is highly sensitive (<0.5 pg S/sec) with equimolar linear response over five orders of magnitude (per sulfur atom). Because there is interest in quantitative determination of both sulfur concentration and species, an altered form of ASTM method D-5623 was used to run various fuel samples and sulfur standards in order to determine total sulfur concentration and composition. In the altered method the GC oven was set to force the sample to elute in short time frames to produce a single sulfur peak. This method helps to eliminate measurement errors encountered by summing individual speciated peaks.

Early results using the SCD showed difficulty in achieving equimolar response. Choice of sulfur species for standardization was shown to be critical to producing equimolar and repeatable results. For instance, hydrogen sulfide (H_2S) is commonly used in the food industry with SCDs to standardize results between laboratories. Due to the volatile nature of H_2S, its reactivity, and the automated sample introduction into the GC, equimolar response became difficult for AFRL to achieve using this standard. However, by using less volatile sulfur species for standardization and making a substitution of pure oxygen for compressed air in the Sievers system, AFRL was able to produce repeatable equimolar response. Based on this success, an extensive evaluation of sulfur standards was conducted at AFRL using Certified Standards from commercial sources, as well as laboratory made standards. This allowed for the measurement of the full spectrum of sulfur concentrations and species typically found in hydrocarbon fuels.

The total sulfur count of each of the fuels tested at AFRL were determined using the altered ASTM Method D-5623and are shown in Figure 3. As expected, it was found that ultra-low RP-1 and JP-7 contained the lowest sulfur concentrations, followed by TS-5, RP-1 standard grade, and TS-30. The JP-8+100 samples had the highest level of sulfur of all hydrocarbon fuels analyzed .

For speciation, the standard ASTM D-5623 method was used. It is useful to note that comparisons between the altered (total sulfur peak) method and the standard (speciated sulfur peaks) method for total sulfur concentrations compare favorably as seen in Table 4. The results of speciation for the various grades of RP-1 tested are summarized in Table 5. Two main types of sulfur compounds – thiophenes (majority) and sulfides were found in the tested grades of RP-1.

Sulfur Compounds	ASTM D-5623 Retention Times[7]	Altered ASTM D-5623 Retention Times	Standard ASTM D-5623 Retention Times
Hydrogen Sulfide	0.95	1.07	
Carbonyl Sulfide	1.21		
Sulfur Dioxide	1.34		
Methanethiol	3.43	0.99, 1.68	
Ethanethiol	7.2	1.04, 1.70	5.51
Dimethyl Sulfide	7.76		
Carbon Disulfide	8.24		6.63
2-Propanethiol	8.92	1.09,1.7, 1.9	7.25
2-Methyl-2-Propanethiol	10.04		8.42
1-Propanethiol	10.42	1.1, 1.2	8.85
Ethylmethyl Sulfide	10.53		9.02
2-Butanethiol	12.01		10.58
Thiophene	12.04		
2-Methyl-1-Propanethiol	12.18		10.91
Diethyl Sulfide	12.82	1.7, 1.8	
1-Butanethiol	13.33		11.87
Dimethyl Disulfide	13.9	1.6-1.9	
2-Methylthiophene	14.71		13.81
3-Methylthiophene	14.84	2.17	
Diethyl Disulfide	17.89	3.12	16.94
Methylbenzothiophene	24.55	8.45	
Methylbenzothiophene	24.66		
Methylbenzothiophene	24.77		
Methylbenzothiophene	24.88		
Diphenyl Sulfide	28.64	12.26	35.19

Table 4: Sulfur Species Retention Times obtained using ASTM Method D-5623

	Halterman UL	TS-5	TS-30	RP-1 Standard	JP-7	JP-10	JP-8 + 10
PPM Sulfur from Altered ASTM D-5623 tested Dec03	0.017		19.9	17.9	0.3		
PPM Sulfur from Standard ASTM D-5623 tested Jun04	0.032	3.5	19	17	0.15	0.08	203
Specie of Sulfur from Standard ASTM D-5623 tested Jun04 Majority	Thiophenes	Thiophenes	Thiophenes	Thiophenes	Thiophenes	Thiophenes	Thiophenes
Specie of Sulfur from Standard ASTM D-5623 tested Jun04 Minority		Sulfides	Sulfides	Sulfides			Mercaptans/Sulfides
Presence of Mercaptan from Standard ASTM D-5623 Yes/No	No	No	No	No	No	No	Yes

Table 5: Total Sulfur Count and Speciation from ASTM Method D-5623

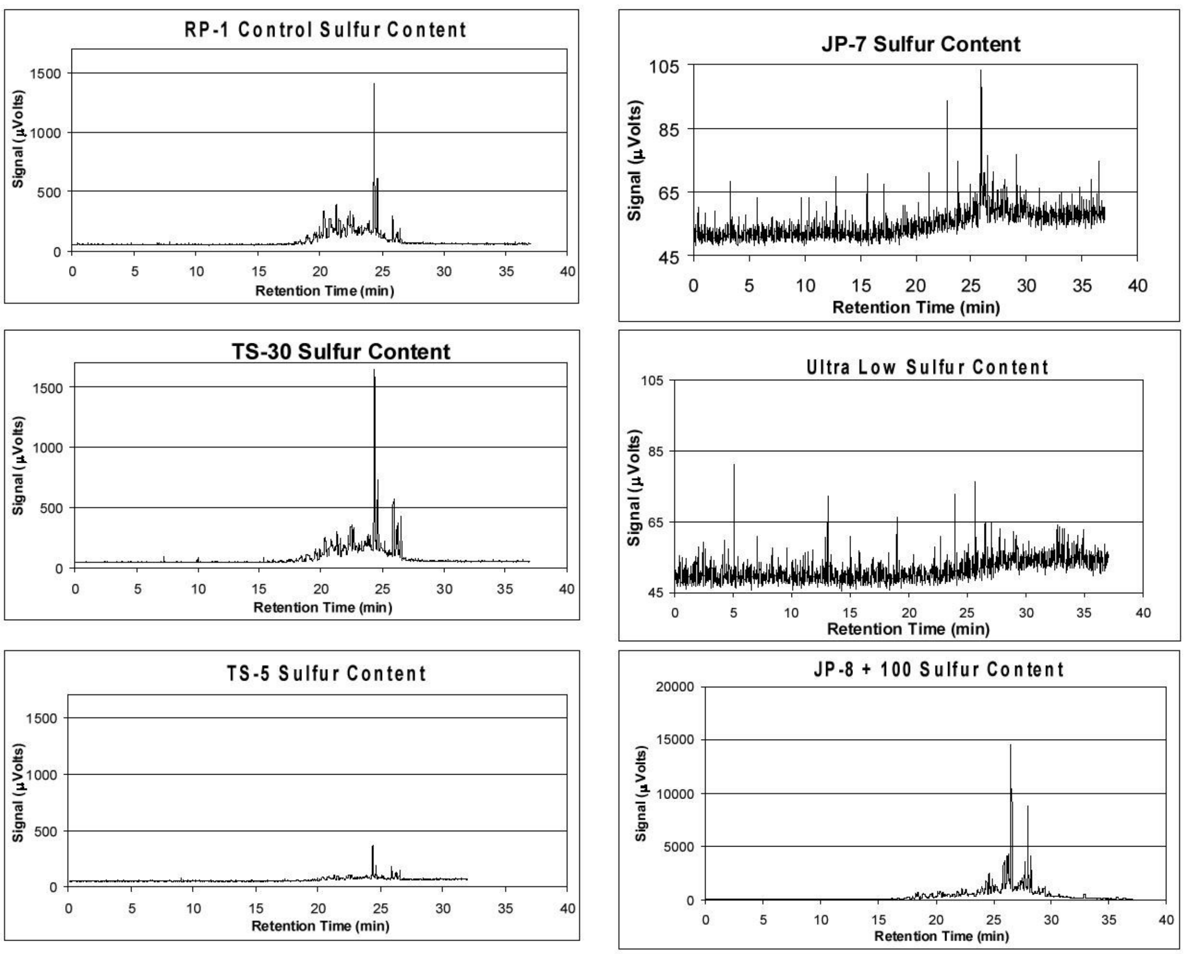


Figure 8: Sulfur Chromatograms from the ASTM D-5623 SCD for the Various Fuels

Future Work

Proposed future work for studying sulfur contamination of RP-1 includes quantifying both total sulfur and reactive species contained within the fuel. Facilities such as NASA Glenn's HTF and AFRL's HHFF will allow for simulative testing of fuel behavior at modern rocket engine conditions. These facilities also will have the capability to help establish an acceptable sulfur limit for use in future engines. If the new sulfur limits can be inexpensively and easily achieved during the fuel refinement process, rocket engine life will be extended, maintenance costs due to repair and upkeep of cooling channels will decrease, and overall engine efficiency will improve over the duration of the mission.

Summary

Both NASA and the Air Force have begun investigating new technology to develop highly efficient, long life, reusable liquid hydrocarbon engines. In order to achieve these goals, a more complete understanding of hydrocarbon fuels, especially RP-1's, thermal stability and chemical composition is required. History has shown that there is a corrosion problem inherent with using Standard Grade RP-1 with copper engine materials, causing decreased engine efficiency and mission life. Several facilities have been used to study higher end sulfur limits, but little research has been performed on establishing a lower, more acceptable sulfur limit for the propellant. If an optimum sulfur limit was established, significant rocket engine system benefits could be realized. In order to begin studying sulfur limits in RP-1, three new grades of RP-1 were formulated to characterize effects of sulfur content. Production feasibility of the altered fuels is still under review. These new grades of RP-1 were tested at NASA Glenn's HTF with expected results. Further work, both from the manufacturing and experimental aspects, is required to establish a firm baseline of acceptable sulfur contamination before current grade RP-1 can be replaced as the common rocket propellant.

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